Docket No.: OGOSH34USA

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.	:	10/540,638	Confirmation No. 5367
Applicant	:	Yasuhiro Yamakoshi	
371 Filed	:	June 23, 2005	
Art Unit	:	1793	
Examiner	:	Vanessa T. Velasquez	
Customer No.	:	00270	
Title	:	NICKEL ALLOY SPUTTERING TARGET	

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VERIFICATION OF TRANSLATION

Sir:

I, Isamu Ogoshi, having been warned that willful false statements and the like are punishable by fine or imprisonment or both, under section 1001 of Title 18 of the United States Code, and may jeopardize the validity of the above-captioned application and any patent issuing thereon, declare:

(1) I am a patent attorney authorized to practice law in Japan and am engaged in the practice of law with OGOSHI International Patent Office at Daini-Toranomon Denki Bldg. 5F, 3-1-10 Toranomon, Minato-ku, Tokyo 105-0001 Japan.

(2) I am fluent in the Japanese and English Languages.

(3) I have reviewed the attached translation, and certify that it is an accurate English translation of the Japanese patent application of Yasuhiro Yamakoshi filed on January 10, 2003 given Japanese Application No. 2003-004685.

(4) All of the statements made herein of my own knowledge are true and all statements made herein on information and belief are believed to be true.

June 19, 2009 Isamu Ogoshi

Date Isamu Ogoshi

DESCRIPTION

NICKEL ALLOY SPUTTERING TARGET

TECHNICAL FIELD

The present invention relates to a nickel alloy sputtering target enabling the formation of a thermally stable silicide (NiSi) film, having favorable plastic workability to the target, and which is particularly effective in the manufacture of a gate electrode material (thin film), as well as to the manufacturing method thereof.

BACKGROUND ART

In recent years, the use of NiSi film in the salicide process as the gate electrode material is attracting attention. Nickel, in comparison to cobalt, is characterized in that it is capable of forming a silicide film with less consumption of silicon during the salicide process. Further, NiSi, as with a cobalt silicide film, is characterized in that the increase of fine wire resistance pursuant to the miniaturization of wiring is unlikely to occur.

In light of the above, nickel is being used instead of the expensive cobalt as the gate electrode material.

Nevertheless, in the case of NiSi, it can easily make a phase transition to the more stable $NiSi_2$, and there is a problem of the boundary roughness becoming aggravated and highly resistive. Moreover, there are other problems in that the film is easily coagulated and excessive formation of silicides may occur.

Conventionally, as technology of using a nickel silicide film or the like,

there is technology of capping and annealing a metal compound film such as TiN on a Ni or Co film to prevent the formation of an insulation film by reacting with oxygen at the time of forming the silicide film. Here, TiN is used in order to prevent the formation of an irregular insulation film by the reaction of oxygen and Ni.

When the irregularity is small, since the length from the NiSi film to the connection of the source/drain diffusion layer will be long, it is said that the connection leak can be suppressed. In addition, TiC, TiW, TiB, WB_2, WC, BN, AlN, Mg_3N_2, CaN, Ge_3N_4, TaN, $TbNi_2$, VB_2, VC, ZrN, ZrB and the like are also disclosed as the cap film (c.f. Japanese Patent Laid-Open Publication No. H7-38104).

Further, with conventional technology, problems have been indicated in that NiSi is easily oxidized even within the silicide material, large irregularities are formed on the boundary area of the NiSi film and Si substrate, and a connection leak will occur.

Here, a proposal has been made for sputtering a TiN film on the Ni film as a cap film, and subjecting this to heat treatment so as to nitride the surface of the NiSi film. This aims to prevent the NiSi from oxidizing, and suppress the formation of irregularities.

Nevertheless, since the nitride film on the NiSi formed by accumulating TiN on Ni is thin, there is a problem in that it is difficult to maintain the barrier properties for a long period of time.

Thus, a proposal has been made of forming the silicide film under a mixed gas (2.5 to 10%) atmosphere with nitrogen gas added thereto so as to make the roughness of the silicide film 40nm or less, and the grain size 200nm or more. Here, it is desirable to cap one among Ti, W, TiNx and WNx on Ni.

Here, it is also described that Ni may be sputtered with argon gas only

without containing nitrogen gas, subsequently sputtering the cap film of TiN, and thereafter injecting N ion in Ni film in order to add N in the Ni film (c.f. Japanese Patent Laid-Open Publication No. H9-153616).

Further, as conventional technology, a semiconductor device and the manufacturing method are disclosed, and the combination of primary metals: Co, Ni, Pt or Pd and secondary metals: Ti, Zr, Hf, V, Nb, Ta or Cr is described. In the Examples, the Co-Ti combination is used.

Cobalt has a lower capability of reducing the silicon oxide film in comparison to titanium, and the silicide reaction will be inhibited if there is natural oxide film existing on the silicon substrate or polysilicon film surface upon accumulating cobalt. Further, the heat resistance properties are inferior to a titanium silicide film, and problems have been indicated in that the heat upon accumulating the silicon oxide film as the interlayer film after the completion of the salicide process causes the coagulation of the cobalt disilicide ($CoSi_2$) film and the resistance to increase (c.f. Japanese Patent Laid-Open Publication No. H11-204791 (USP5989988)).

Further, as conventional technology, there is a disclosure of a “manufacturing method of a semiconductor device”, and technology is described for where a layer of an amorphous alloy with a metal selected from a group consisting of titanium Ti, zirconium Zr, tantalum Ta, molybdenum Mo, niobium Nb, hafnium Hf, and tungsten W is deposited on a surface as a layer containing cobalt Co or nickel N in order to prevent the short-circuit caused by the overgrowth upon forming salicide. Here, although there are Examples that show a cobalt content of 50 to 75at% and Ni40Zr60, the alloy content is large for making an amorphous layer (c.f. Japanese Patent Laid-Open Publication No. H5-94966).

As described above, all of the disclosed conventional technology relate to the deposition process, and do not relate to a sputtering target.

Further, with the conventional high purity nickel, the purity was roughly up to 4N excluding gas components, and the oxygen was high at roughly 100ppm.

As a result of manufacturing a nickel alloy target based on this kind of conventional nickel, plastic workability was inferior and it was not possible to manufacture a high quality target. Also, there was a problem in that numerous particles were generated during sputtering, and the uniformity was inferior.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a nickel alloy sputtering target, and the manufacturing technology thereof, enabling the formation of a thermally stable silicide (NiSi) film, unlikely to cause the coagulation of films or excessive formation of silicides, having few generation of particles upon forming the sputtered film, having favorable uniformity and superior in the plastic workability to the target, and which is particularly effective for the manufacture of a gate electrode material (thin film).

In order to achieve the foregoing object, the present inventors discovered that a target enabling the formation of a thermally stable silicide (NiSi) film, having few generation of particles during sputtering, having favorable uniformity and superior in plastic workability by adding specific metal elements to high purity nickel.

Based on the foregoing discovery, the present invention provides:

1. A nickel alloy sputtering target containing 0.5 to 10at% of tantalum in nickel;

2. A nickel alloy sputtering target containing 1 to 5at% of tantalum in nickel;

3. A nickel alloy sputtering target according to paragraph 1 or paragraph 2 above, wherein inevitable impurities excluding gas components are 100wtppm or less;

4. A nickel alloy sputtering target according to paragraph 1 or paragraph 2 above, wherein inevitable impurities excluding gas components are 10wtppm or less;

5. A nickel alloy sputtering target according to any one of paragraphs 1 to 4 above, wherein oxygen is 50wtppm or less, and nitrogen, hydrogen and carbon are respectively 10wtppm or less;

6. A nickel alloy sputtering target according to any one of paragraphs 1 to 5 above, wherein oxygen is 10wtppm or less;

7. A nickel alloy sputtering target according to any one of paragraphs 1 to 6 above, wherein the initial magnetic permeability of in-plane direction of the target is 50 or more;

8. A nickel alloy sputtering target according to any one of paragraphs 1 to 7 above, wherein the maximum magnetic permeability on the initial magnetization curve of the in-plane direction of the target is 100 or more;

9. A nickel alloy sputtering target according to any one of paragraphs 1 to 8 above, wherein the average crystal grain size of the target is 80 μm or less; and

10. A manufacturing method of a nickel alloy sputtering target according to any one of paragraphs 1 to 9 above, wherein final heat treatment is performed at a recrystallization temperature of up to 950°C.

BEST MODE FOR CARRYING OUT THE INVENTION

The target of the present invention is made to be a high purity nickel alloy ingot by performing electrolytic refining to rough Ni (up to roughly 4N),

removing the metal impurity components, and further refining this with EB melting in order to obtain a high purity nickel ingot. Then, this ingot and high purity tantalum are subject to vacuum melting to prepare a high purity nickel alloy ingot.

Upon performing vacuum melting, the cold crucible melting method employing a water-cooled copper crucible is suitable. This alloy ingot is cast, rolled and subject to other processes to form a plate shape, and ultimately subject to heat treatment at a recrystallization temperature about 500°C to 950°C to prepare a target. The analytical values of this representative high purity nickel target are shown in Table 1.

Table 1

Element	(wtppm)	Element	(wtppm)
Li	<0.001	Ag	<0.01
Be	<0.001	Cd	<0.01
B	0.02	In	<0.05
F	<0.01	Sn	0.2
Na	<0.01	Sb	<0.01
Mg	0.57	Te	<0.01
Al	0.14	I	<0.01
Si	2.7	Cs	<0.01
P	<0.01	Ba	<0.005
S	0.02	La	<0.005
Cl	<0.01	Ce	<0.005
K	<0.01	Pr	<0.005
Ca	<0.01	Nd	<0.005
Sc	<0.001	Sm	<0.005
Ti	0.24	Eu	<0.005
V	0.01	Gd	<0.005
Cr	0.02	Tb	<0.005
Mn	0.12	Dy	<0.005
Fe	1	Ho	<0.005
Co	0.66	Er	<0.005
Ni	Matrix	Tm	<0.005
Cu	0.13	Yb	<0.005
Zn	<0.01	Lu	<0.005
Ga	<0.01	Hf	<0.01
Ge	<0.05	Ta	10.01
As	<0.01	W	0.02
Se	<0.01	Re	<0.01
Br	<0.05	Os	<0.01
Rb	<0.005	Ir	<0.01
Sr	<0.005	Pt	0.07
Y	<0.005	Au	<0.01
Zr	<0.01	Hg	<0.01
Nb	0.2	Tl	<0.01
Mo	0.03	Pb	0.04
Ru	<0.01	Bi	<0.005
Rh	<0.01	Th	<0.0001
Pd	<0.01	U	<0.0001
		H	<10
		C	<10
		N	<10
		O	<10

Note: Pursuant to GDMS analysis excluding H, C, N, O and Ta
Note: Ta is wt%
Note: < means less than measuring limit

The additive amount of tantalum is 0.5 to 10at%, more preferably 1 to 5at%. If the additive amount is too small, the thermal stability of the nickel alloy layer cannot be improved. If the additive amount is too great, the film resistance will become so large that it will be inappropriate, and there is a problem in that the amount of intermetallic compounds will increase and make the plastic processing difficult, and the generation of particles during sputtering will also increase.

As a result of performing sputtering with the tantalum-added nickel alloy of the present invention, heating this sputtered film under a nitrogen atmosphere, and thereafter measuring the temperature of change in the crystal structure with the XRD diffraction method, the phase change temperature of 50 to 90°C improved due to the addition of tantalum, and apparent thermal stability could be confirmed.

In order to reduce the generation of particles during sputtering and to improve the uniformity, it is desirable to make the inevitable impurities excluding gas components 100wtppm or less, and more preferably 10wtppm or less.

Further, since gas components will also cause the increase in the generation of particles, it is desirable to make the content of oxygen 50wtppm or less, more preferably 10wtppm or less, and the contents of nitrogen, hydrogen and carbon respectively 10wtppm or less.

It is important to make the initial magnetic permeability of the target 50 or more (preferably around 100), and the maximum magnetic permeability 100 or more with respect to the sputtering characteristics.

Final heat treatment is performed at a recrystallization temperature about 500°C to 950°C to form a substantial recrystallization texture. If the heat treatment temperature is less than 500°C, sufficient recrystallization texture cannot be obtained. Further, the permeability and maximum magnetic

permeability cannot be improved.

In the target of the present invention, although the slight existence of non-recrystallization will not affect the characteristics, a significant amount of such existence is not preferable. It is desirable that the average crystal grain size of the target is 80 μm or less.

A final heat treatment exceeding 950°C is not preferable as this will enlarge the average crystal grain size. When the average crystal grain size is enlarged, the variation of the crystal grain size will increase, and the uniformity will deteriorate.

Examples and Comparative Examples

The present invention is now described with reference to the Examples and Comparative Examples. These Examples are merely illustrative, and the present invention shall in no way be limited thereby. In other words, the present invention shall only be limited by the scope of claim for a patent, and shall include the various modifications other than the Examples of this invention.

(Example 1-1 to Example 3-2)

Rough Ni (up to roughly 4N) was subject to electrolytic refining, metal impurity components were removed, this was further refined with EB melting in order to obtain a high purity nickel ingot, and this ingot and high purity tantalum were subject to vacuum melting in order to manufacture a high purity nickel alloy ingot. Upon performing vacuum melting, the cold crucible melting method employing a water-cooled copper crucible was used.

This alloy ingot was cast, rolled and subject to other processes to form a plate shape, and ultimately subject to heat treatment at a recrystallization temperature about 500°C to 950°C to prepare a target.

The manufacturing conditions of the target; namely, the Ta amount, purity, oxygen content, and heat treatment temperature conditions, as well as the characteristics of the target and deposition; namely, the initial magnetic

permeability, maximum magnetic permeability, average crystal grain size, variation of the crystal grain size, particle amount, and uniformity are shown in Table 2.

As shown in Table 2, Example 1 series has a Ta amount of 1.68at%, Example 2 series has a Ta amount of 3.48at%, and Example 3 series has a Ta amount of 7.50at%.

Table 2

	Ta Volume (at%)	Purity	Oxygen (wtppm)	Heat Treatment Conditions (℃) x 1hr	Initial Magnetic Permeability	Maximum Magnetic Permeability	Average Grain Size (μ m)	Variation (%)	Particles (0.3 μ m or more/in^2)	Uniformity (%,3 σ)
Example 1-1	1.68	5N	35	500	62	103	Non-recrystallization Found	-	23	8
Example 1-2	1.68	5N	25	600	103	142	Non-recrystallization Found	-	18	11
Example 1-3	1.68	5N	<10	650	121	165	17.3	9.6	15	7
Comparative Example 1-1	1.68	3N5	80	650	118	161	7.1	8.2	113	5
Comparative Example 1-2	1.68	4N	75	650	115	167	8.5	7.6	103	3
Comparative Example 1-3	1.68	5N	<10	300	18	47	No Recrystallization	-	20	7
Comparative Example 1-4	1.68	5N	<10	450	23	63	Non-recrystallization Found	-	18	18
Comparative Example 1-5	1.68	5N	<10	1000	141	189	244	57	15	14
Example 2-1	3.48	5N	<10	750	67	118	Non-recrystallization Found	-	17	11
Example 2-2	3.48	5N	<10	800	102	156	12.7	18	9	6
Example 2-3	3.48	5N	<10	850	112	163	53.2	21	12	13
Example 2-4	3.48	5N	<10	930	121	165	73.4	27	15	11
Comparative Example 2-1	3.48	3N5	<10	300	11	29	No Recrystallization	-	47	8
Comparative Example 2-2	3.48	4N	<10	650	16	59	Non-recrystallization Found	-	55	21
Comparative Example 2-3	3.48	5N	<10	1050	125	166	153	43	16	23
Comparative Example 2-4	3.48	5N	<10	1150	124	172	146	51	19	27
Example 3-1	7.50	5N	<10	900	67	123	46	11	37	15
Example 3-2	7.50	5N	<10	950	75	131	68	19	42	13
Comparative Example 3-1	7.50	5N	<10	600	13	41	Non-recrystallization Found	-	43	26
Comparative Example 3-2	7.50	5N	<10	1250	81	135	213	33	51	21

Examples 1-1 to 1-3, Examples 2-1 to 2-4 and Examples 3-1 to 3-2 in which the Ta amount, purity, oxygen content, and heat treatment temperature conditions are within the scope of the present invention had an initial magnetic permeability of 50 or more, a maximum magnetic permeability of 100 or more, an average crystal grain size of 80 μm or less, the variation of the crystal grain size was small, the particle amount (0.3 μm or more/in^2) was also small, and the uniformity (%, 3 σ) was also a small value.

As a result of performing sputtering with the tantalum-added nickel alloy of the present Examples, heating this sputtered film under a nitrogen atmosphere, and thereafter measuring the temperature of change in the crystal structure with the XRD diffraction method, the phase change temperature of 50 to 90°C improved due to the addition of tantalum, and apparent thermal stability could be confirmed.

Incidentally, since the heat treatment temperature was slightly low in Example 1-1, Example 1-2 and Example 2-1, there were some non-recrystallized textures, but since the existence thereof was small, the characteristics were not affected.

(Comparative Example 1-1 to 3-2)

The manufacture process was the same as the foregoing Examples, and the additive amount of Ta was also the same, but the conditions of purity, oxygen content and heat treatment temperature were changed as shown in Table 2 upon manufacturing the target. The characteristics of the target and deposition; namely, the initial magnetic permeability, maximum magnetic permeability, average crystal grain size, variation of the crystal grain size, particle amount, and uniformity were measured and observed.

Incidentally, as with the Examples, Comparative Example 1 series has a Ta amount of 1.68at%, Comparative Example 2 series has a Ta amount of 3.48at%, and Comparative Example 3 series has a Ta amount of 7.50at%.

As a result, Comparative Examples 1-1 and 1-2 has significant amounts of oxygen, and, since the purity is low, there was a problem in that many particles were generated. Since the heat treatment temperature is too low in Comparative Examples 1-3 and 1-4, the initial magnetic permeability and maximum magnetic permeability could not be improved, and this could not be recrystallized, or large amounts of non-recrystallized textures existed.

Since the final heat treatment temperature was too high in Comparative Example 1-5, the average crystal grain size enlarged, the variation increased, and the uniformity deteriorated.

Since the purity was low and the heat treatment temperature was too low in Comparative Example 2-1 and Comparative Example 2-2, the initial magnetic permeability and maximum magnetic permeability could not be improved, and this could not be recrystallized, or large amounts of non-recrystallized textures existed. Numerous particles were also generated.

Since the final heat treatment temperature was too high in Comparative Examples 2-3 and 2-4, the average crystal grain size enlarged, the variation increased, and the uniformity deteriorated.

Since the heat treatment temperature was low in Comparative Example 3-1, the initial magnetic permeability and maximum magnetic permeability could not be improved. Large amounts of non-recrystallized textures existed, and numerous particles were also generated.

Since the final heat treatment temperature was too high in Comparative Example 3-2, the average crystal grain size enlarged, the variation increased, and the uniformity deteriorated.

Effect of the Invention

As described above, a nickel alloy sputtering target containing a prescribed amount of tantalum in nickel yields a superior effect in that it

enables the formation of a thermally stable silicide (NiSi) film, is unlikely to cause the coagulation of films or excessive formation of silicides, has few generation of particles upon forming the sputtered film, has favorable uniformity and is superior in the plastic workability to the target, and is particularly effective for the manufacture of a gate electrode material (thin film).

CLAIMS

1. A nickel alloy sputtering target containing 0.5 to 10at% of tantalum in nickel.

2. A nickel alloy sputtering target containing 1 to 5at% of tantalum in nickel.

3. A nickel alloy sputtering target according to claim 1 or claim 2, wherein inevitable impurities excluding gas components are 100wtppm or less.

4. A nickel alloy sputtering target according to claim 1 or claim 2, wherein inevitable impurities excluding gas components are 10wtppm or less.

5. A nickel alloy sputtering target according to any one of claims 1 to 4, wherein oxygen is 50wtppm or less, and nitrogen, hydrogen and carbon are respectively 10wtppm or less.

6. A nickel alloy sputtering target according to any one of claims 1 to 5, wherein oxygen is 10wtppm or less.

7. A nickel alloy sputtering target according to any one of claims 1 to 6, wherein the initial magnetic permeability of in-plane direction of the target is 50 or more.

8. A nickel alloy sputtering target according to any one of claims 1 to 7, wherein the maximum magnetic permeability on the initial magnetization curve of the in-plane direction of the target is 100 or more.

9. A nickel alloy sputtering target according to any one of claims 1 to 8, wherein the average crystal grain size of the target is 80 μm or less.

10. A manufacturing method of a nickel alloy sputtering target according to any one of claims 1 to 9, wherein final heat treatment is performed at a recrystallization temperature of up to 950°C.

ABSTRACT

A nickel alloy sputtering target containing 0.5 to 10at% of tantalum in nickel, in which inevitable impurities excluding gas components are 100wtppm or less. Provided is a nickel alloy sputtering target, and the manufacturing technology thereof, enabling the formation of a thermally stable silicide (NiSi) film, unlikely to cause the coagulation of films or excessive formation of silicides, having few generation of particles upon forming the sputtered film, having favorable uniformity and superior in the plastic workability to the target, and which is particularly effective for the manufacture of a gate electrode material (thin film).